

High Voltage Stability and Enhanced Electrochemical Performances of LiCoO_2 by CeF_3 Coating

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Abstract— Surface coating of LiCoO_2 remained one of the efficient methods to enhance its electrochemical and thermal performances, especially at high cut-off potential. For several years, REMINEX research center has worked on the development of cathode materials for lithium batteries. Recently, a patent was published on a new cathode materials based on Ce doped- LiCoO_2 . Based on previous works and our know-how on cerium chemistry, we developed LiCoO_2 coating using Ce-based compounds. In this work, CeF_3 coated LiCoO_2 was synthesized via solid state reaction of cobalt oxide and lithium carbonates followed by precipitation of CeF_3 in presence of lithium cobalt oxide powder. The morphology and structure of the modified cathode material were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results show the disappearance of the Hexagonal-Monoclinic transition around 4.1V by coating. This transition contributes indeed in the structural instability of bare- LiCoO_2 . the fluoride compound CeF_3 is successfully coated on the surface of LiCoO_2 cathode particles with an average layer thickness about 40 nm.

The electrochemical tests show that the CeF_3 -coating layer significantly enhances the cycling performance of LiCoO_2 cathode material, even at high cut-off potential. While the bare LiCoO_2 cathode displays fast fading at 4.6 V vs. Li^+/Li cutoff potential, the surface-modified electrode exhibits the great capacity of 160 mAh/g with an excellent capacity retention on several cycles. The thermal stability of coated LiCoO_2 was also improved by the surface modification.

We concluded that the electrochemical and the thermal enhancement at high potential are ascribed to the presence of CeF_3 coating layer which prevents the side reaction during the charge discharge process, alleviate the attack by the acidic electrolyte and reduce the damage of electrode structure.

Keywords- *Li-ion batteries; Lithium cobalt oxide; metal fluoride coating; cerium fluoride; high voltage; cathode materials*

I. INTRODUCTION

Lithium ion batteries have attracted considerable interest because of the promising application ranging from electronic devices, to the electric and hybrid vehicles or space applications. Total sales of the cells in 2013 have been reported

to be over 17.5 billion dollars, and are expected to be more than quadruple by 2020.

Since the first Li-ion battery commercialized by Sony, layered LiCoO_2 is still the most widely used commercial cathode material because of its high electronic conductivity, excellent cycling performances, low self-discharge rate and excellent capacity retention below 4.2 V (vs. Li^+/Li), reasonable rate capability and feasible recycling from spent batteries [1-3].

In spite of a high theoretical specific capacity of 274mAh/g, the practical reversible capacity of LiCoO_2 is limited to only 140 mAh/g or less when cycled between 3.0 and 4.2 V (vs. Li^+/Li) in order to maintain a reasonable cycling stability [4]. By charging to higher voltage such as 4.5 V, the capacity of the cell will increase by about 20%. However, its capacity fades sharply because of side reactions with the electrolyte at high potentials as well as structural instability induced by a phase transition. The boost in the cell capacity also leads to an increase in safety concerns.

To overcome this problem, many approaches are adopted in the literature, either by the modification of the LiCoO_2 particle surface with a metal oxide [5-7] or fluorine compounds [8,9], or either by the partial substitution of Co by other metals in LiCoO_2 [10].

Several different mechanisms have been suggested for the improvement of electrochemical stability of cathode material by metal oxide coating, such as: (1) reduction of “electrolyte–electrode” interactions; (2) formation of the solid solution between metal oxides and layered oxides near the particle surface; (3) creation of stable grain boundaries by formation of composite two-phase cathodes; (4) improving of thermal stability of oxides in delithiated state.

There are many suitable coating materials, such as metal oxides (MgO [11,12], Al_2O_3 [13], SnO_2 [14], SiO_2 [15], ZrO_2 [16], ZnO [17]) and phosphoric salt AlPO_4 [18-21]. The results demonstrated promising increases in the discharge capacity reversibility upon cycling; however, the resulting thermal properties remained unimproved due to the intrinsic structural instability of the parent LiCoO_2 at a highly delithiated state and most of the metal oxides as coating materials cannot remain

stable under the corrosion of HF from the electrolyte (degradation of LiPF_6 salt).

In recent years, fluorine in the form of metal fluorides such as AlF_3 [22], CaF_2 [23], MgF_2 [24], LaF_3 [25], CeF_3 [26], FeF_3 [27] is considered to be one of the most promising coating materials to improve electrochemical performance of cathode, due to its high stability. This could be attributed to the reduction of the structural change of active material from HF attack by a thin coating layer preventing the direct contact between delithiated cathode and liquid electrolyte.

In this paper, we have attempted to synthesize CeF_3 -coated LiCoO_2 particles by precipitation method. The effect of coating on the structural, electrochemical and thermal properties was investigated in detail. The CeF_3 -coated LiCoO_2 cathode material exhibits the highly enhanced cycling performance and rate capability compared with the pristine at high cut off voltage (4.5 V). The thermal properties are enhanced compared with standard LiCoO_2 .

II. EXPERIMENTS

II.1. Preparation of CeF_3 coated LiCoO_2 materials

LiCoO_2 powder was prepared by employing Co_3O_4 (Managem group S.A. product) and Li_2CO_3 (Aldrich) powders as starting materials. The both reagents were mixed in the mole ratio of 1:1.05 and fired under air at 900 °C. Excess Li_2CO_3 was used to compensate for the loss of Li during firing. The obtained LiCoO_2 was used for CeF_3 coating as presented in the flow chart at figure 1.

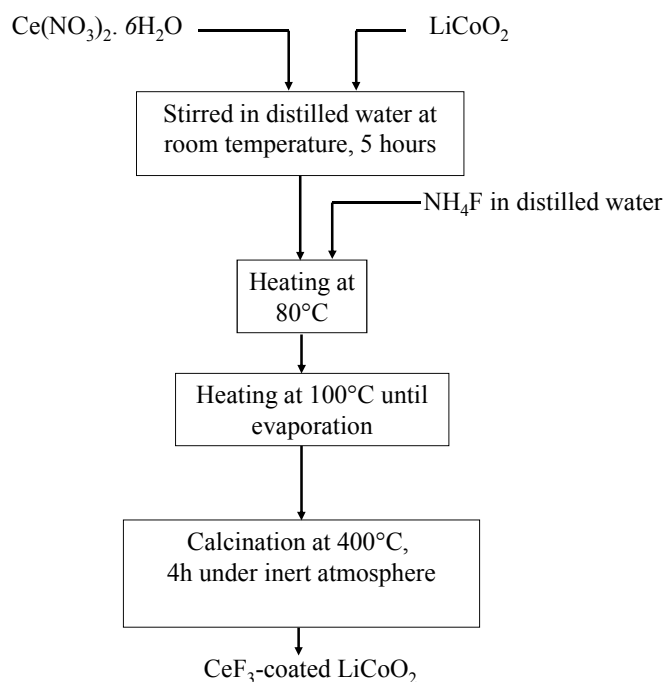


Figure 1. Flow chart for the CeF_3 -coated LiCoO_2 cathode materials prepared by a co-precipitation process

In the preparation of CeF_3 -coated LiCoO_2 , cerium nitrate octahydrate and ammonium fluoride were separately dissolved

in distilled water firstly. LiCoO_2 powder was dispersed in the solution containing cerium nitrate and stirred for 5h to obtain a homogeneous suspension. Then, the stoichiometric amount of ammonium fluoride was added drop by drop to the mixture under heating at 80°C. After filtration, the precipitate was washed several times with distilled water in order to eliminate residual ammonium nitrates. The resulting powders were heat-treated in a furnace at 400 °C for 4 h under inert atmosphere.

II.2. Physical characterization

The X-ray diffraction (XRD, Philips X-pert) with monochromatic $\text{Cu-K}\alpha$ radiation was employed to identify the crystal structure of the powders in the 2θ range from 10 to 60°, with a step size of 0.03°. Structural parameters, such as lattice constants and intensity ratio, were calculated by Dopowder program.

Scanning electron microscope (SEM, FEI) and transmission electron microscope (TEM, TECNAI G2/FEI) were used to observe the micromorphology of the powders and the status of coating layer. Energy dispersive spectroscopy (EDS) was employed to analyze the surface composition and the element content of powders.

The thermal stability of bare and coated- LiCoO_2 materials was evaluated by differential scanning calorimeter (Perkin Elmer DSC 8000) using a temperature scan rate of 5°C/min. The cells were charged to 4.6 V at 400 μA (40 mA/g) and then disassembled in the glove box. The cathode materials were recovered from the current collector after removing the remained electrolyte. Samples of 3-5 mg were collected in a stainless steel sealed pan with a gold plated copper seal. The weight was constant in all cases, indicating that no leaks occurred during the experiments.

II.3. Electrochemical characterization

Electrochemical characterizations of all the synthesized materials were performed using a CR2430 coin cell fabricated in a glove box (Jacomex, SA) under an Argon atmosphere. The cell consisted of the synthesized material as the cathode and a metallic lithium anode separated by a polypropylene microporous film (Celgard 2300) as separator with 1M LiPF_6 dissolved in EC:DMC (1:1 by volume) as the electrolyte.

For cathode fabrication, the prepared powders were mixed with 15 wt.% of black carbon and 10 wt.% of polyvinylidene fluoride (PVDF) in N-methyl pyrrolidinone until slurry was obtained. The blended slurries were cast onto an aluminum current collector by a doctor blade method, and the electrode was dried at 125 °C in vacuum before the fabrication of the cell. All the organic solvents and electrolyte were of battery grade.

Galvanostatic charge/discharge testing was performed at different potential range between 3 V and 4.6 V and at a current density of 40 mA/g on an Arbin BT 2000 battery tester.

III. RESULTS AND DISCUSSION

III.1. X-ray diffraction and refinement parameters

The X-ray diffraction (XRD) patterns of bare LiCoO₂ and CeF₃-coated LiCoO₂ powders are given in Fig. 2. The main peaks confirmed that both materials can be indexed in the hexagonal-type space group R $\bar{3}$ m. The XRD pattern of the CeF₃-coated LiCoO₂ material shows additional peaks attributed to cerium oxide CeO₂. This is presumably because the content of CeF₃ is high (2 % mol) and its excess doesn't form only a thin film on the surface of LiCoO₂ but also an aggregate of cerium oxide. The lattice parameters were calculated by a least square method from Figure 2 and presented in Table 1.

CeF₃-coated LiCoO₂ exhibits larger values of the lattice parameters, in particular for c parameter (c=1.410 nm).

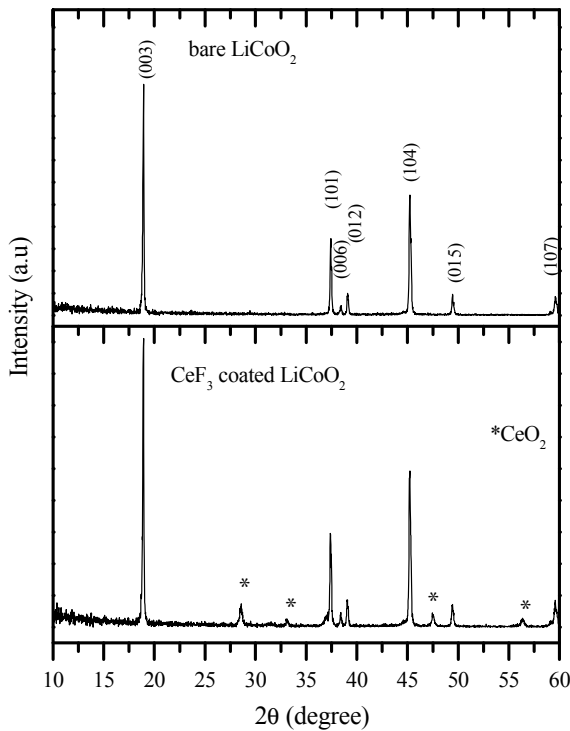


Figure 2. XRD patterns of the bare LiCoO₂ and CeF₃-coated LiCoO₂ powders. The diffraction peaks from LiCoO₂ were indexed in the patterns.

TABLE 1. Cell parameters for bare-LiCoO₂ and CeF₃-coated LiCoO₂

Sample	Lattice constants (nm)		c/a	I ₍₀₀₃₎ /I ₍₁₀₄₎
	a	c		
Bare LiCoO ₂	0.2816 (3)	1.405 (2)	4.993	1.62
CeF ₃ -coated LiCoO ₂	0.2821 (3)	1.410 (2)	4.998	1.85

That suggests the formation of solid solutions incorporating ions with larger crystal ionic radii (Ce³⁺: 0.107 nm, Ce⁴⁺: 0.092

nm and Co³⁺: 0.063 nm). According to these authors [29], the substitution of a tetravalent ion is possible in the interstitial Co⁴⁺ sites. Thus, we expect that an inter-oxide film of composition LiCo_{1-y}Ce_yO₂ is formed on the surface. The presence of nano-sized CeO₂ at the surface of LiCoO₂ can improve the stability of lithium cobalt oxide by its doping effect [10].

The ratio I₀₀₃/I₁₀₄ is sensitive to the cation distribution in lattice and the degree of cation mixing of materials [29-31]. When the ratio is higher, disorder degree of the cations is lower, and the electrochemical performance is relatively better. This ratio is about higher for surface modified LiCoO₂ compared with unmodified material. The highest value (1.85) is showed for CeF₃-coated LiCoO₂ indicating a good layered structure with a small cation mixing.

III.2. Scanning Electron Microscopy

Figure 3 shows the SEM images of uncoated LiCoO₂ and CeF₃-coated LiCoO₂. It can be seen that all materials show the

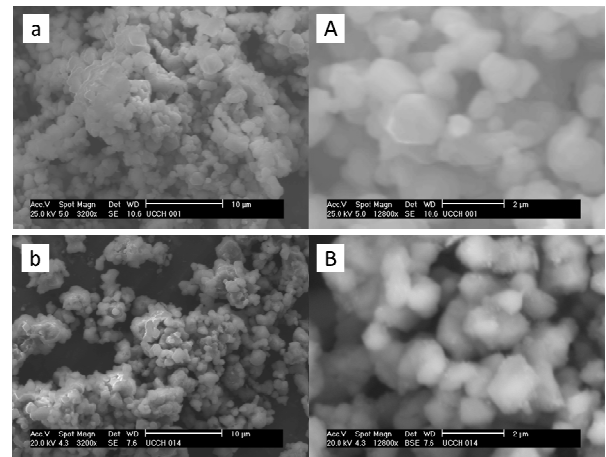


Figure 3. SEM pictures of bare-LiCoO₂ (a, A) and CeF₃-coated LiCoO₂ (b, B) materials at two different magnifications

near-spherical morphology, with a sub-micrometric size distribution. After the coating with CeF₃, the morphology appears rougher with a fine particles dispersed on the surface. May be the amount of fluorides cerium is more than is required to form a thin layer on the cathode material and the excess of coating compound agglomerates into small aggregates on the surface.

III.3. Transmission Electron Microscopy

In order to verify if there is a coating layer, more detail examination by transmission electron microscopy (TEM) analysis was performed. Figure 4 shows a TEM of a typical primary particle from CeF₃-coated LiCoO₂ powders. Magnified images around the edge of the particle clearly reveal that it is encapsulated by a thick coating layer. It has been noticed that the CeF₃-coated LiCoO₂ coating layer seemed to be composed of a thin layer with the thickness of 30-50 nm as well as a small crystalline particles.

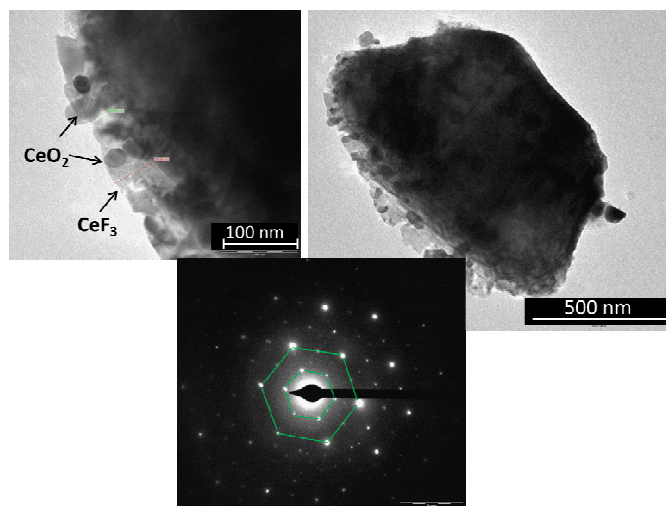


Figure 4. TEM images of the surface of a LiCoO_2 particle and after CeF_3 coating. The lighter region surrounding the particle (darker region) is the coating layer, which is a few nanometers thick in the right picture. The electron diffraction on the surrounded region indicates the hexagonal structure of CeO_2 .

The spot pattern of the right side also shows the coating layer is a mixture of crystalline (or quasi-crystalline) and an amorphous phase. As confirmed by the XRD pattern of Fig. 2, the excess of cerium was oxidized to CeO_2 and forms some individual or (coated aggregates). It is clear that the addition of 2% mol of CeF_3 lead to the formation of agglomerates which glue to the surface. It is also possible that during the calcinations process (400 °C), some oxygen from air have diffused into the furnace, resulting in the oxidation of cerium and making the coating less homogeneous. According to our previous patent [10] the introduction of nano-sized CeO_2 can stabilize the structure of LiCoO_2 by increasing the stability of crystalline structure. In the other side, the presence of CeF_3 coating layer will stabilize the interface and protect the cathode materials against HF attack in electrolyte.

The coating layer could reduce the contact area of active material with the electrolyte and protect the active material from dissolution in the electrolyte.

III.4. Electrochemical characterization and cycling performances

The electrochemical performances of the bare and coated- LiCoO_2 was investigated galvanostatically at room temperature. A CR2430 coin-type halfcells employing Li metal as the anode was used to investigate the specific charge-discharge capacities as a function of charge cut-off voltage and at a constant current density of 40 mA/g (0.2 C rate).

Figure 5 shows cycling performances of the bare and coated- LiCoO_2 cycled with the upper cut-off voltages (4.25, 4.4, and 4.6 V). It is noted that the initial charge capacity for the bare- LiCoO_2 is much higher than that for LiCoO_2 coated cathode. However, they exhibit almost the same discharge capacity as compared to the uncoated material. This is probably due to a suppression of the reaction between the cathode surface and the electrolyte and an optimization of the solid-

electrolyte interface (SEI) layer, which would facilitate the Li^+ ion transportation during discharge process and subsequent cycling.

The data show that all the both cathode materials exhibit a good cycling stability even at higher cut-off voltage (4.4 V).

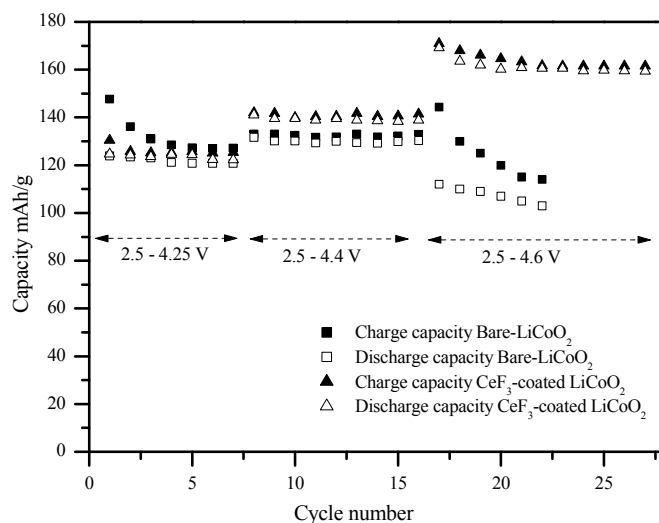


Figure 5. Cycling performances of bare- LiCoO_2 and CeF_3 -coated LiCoO_2 at different potential windows

By increasing the cut-off voltage to 4.6 V, the discharge capacity decreases drastically for the bare- LiCoO_2 while the CeF_3 -coated LiCoO_2 showed a good cycling stability with an increased capacity from 140 mAh/g to 160 mAh/g.

Fig 6 illustrates the voltage-capacity curves for the bare- LiCoO_2 at different cycles cycled with the upper cut-off voltages (4.25, 4.4, and 4.6 V vs Li^+/Li).

The first charge and discharge curves of bare- LiCoO_2 shows typical potential plateaus of hexagonal LiCoO_2 cathode, but with large irreversible capacity (31 mAh/g). By increasing the cutoff potential to 4.6 V, the profiles of the bare LiCoO_2 cathode become larger with a higher potential polarization. The charge discharge curves of CeF_3 coated- LiCoO_2 show good performances, the reversible capacity is higher than those of uncoated cathode. It's interesting to note the low polarization by increasing the cut-off voltage to higher values (4.4 V and 4.6 V).

These results show that charging to 4.6 V vs Li^+/Li was impossible for the cell using the bare LiCoO_2 cathode powder. On the other hand, reversible charge-discharging to 4.6 V vs Li^+/Li was made possible by a coating of CeF_3 , and the discharge capacity was about 160 mAh/g. This value is a high value, about 1.14 times the capacity reported conventionally for standard LiCoO_2 cathode material (3.0-4.2 V vs. Li^+/Li charge-discharge; approximately 140 mAh/g).

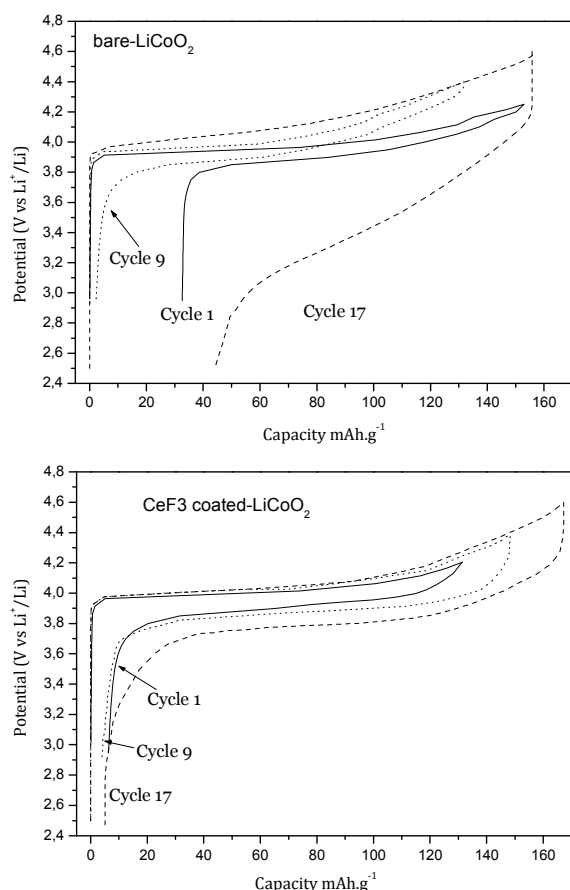


Figure 6. Charge-discharge curves of bare-LiCoO₂ and CeF₃-coated LiCoO₂ at cycle 1 (4.25 V), cycle 9 (4.4 V) and cycle 17 (4.6 V)

III.5. Differential scanning calorimetry (DSC)

To evaluate the reaction between the cathode electrodes and the electrolyte, DSC measurements of the charged electrodes at 4.4 V were carried out. Figure 7 shows the obtained curves.

The bare cathode material displays a characteristic exothermic peak with a thermal decomposition temperature at 208.5 °C and reaction enthalpy of 544.6 J/g, whereas, the CeF₃-coated cathode exhibited an exothermic peak centered at 288.5°C and lower reaction enthalpy of 294 J/g. This result suggests that coating LiCoO₂ with fluoride-Ce compound retards the reaction with the electrolyte.

In the process, the heat evolution is due to the decomposition and destruction of the layered structure with the release of oxygen, because of the instability of the highly oxidized Co⁴⁺ ions in the lattice at a constantly charged state, at high temperatures. The decrease in heat evolution agrees with existing literature on the coated samples compared to the uncoated samples [32-34].

The mechanism for the improved thermal stability could be explained as follows. In comparison with the uncoated material, the CeF₃ coating layer plays an important role in separating the active material and the electrolyte and stabilizing the surface lattice oxygen. The CeF₃-coated delithiated material releases less active oxygen species during heating process. It's

known that cerium acts as an "oxygen reservoir"; this property is known as "OSC" (oxygen storage capacity) allow stabilizing the LiCoO₂ structure [35,36]. The less the active oxygen species releases, the less the reaction occurs between the active oxygen species and the electrolyte remained on the material surface.

As a consequence, the CeF₃-coated cathode materials exhibited considerably less exothermic activity and reduced heat generation at a highly delithiated state, and thereby possessed better thermal safety characteristics than pristine LiCoO₂ cathode materials.

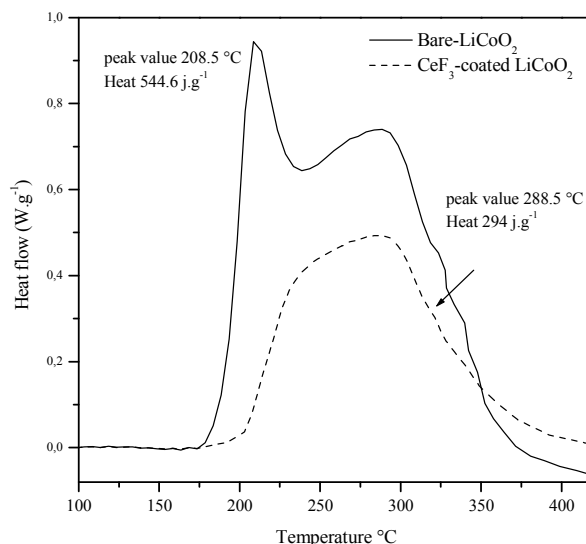


Figure 7. DSC curves of the bare LiCoO₂ and CeF₃-coated LiCoO₂ cathode materials after fully charged at 4.4V vs. Li⁺/Li for 20 h.

CONCLUSION

In summary, the layered LiCoO₂ electrode was prepared and successfully coated with CeF₃ using a simple chemical deposition process. It was shown by XRD and TEM data that the materials form new thin phases on the surface (30 to 50 nm thick) after a solid state reaction.

The coated-LiCoO₂ cathodes had higher polarization than the bare cathode batteries but better electrochemical performances, in particular at high cutoff potential. For CeF₃-coated LiCoO₂, the reversible capacity was about 160 mAh/g at 4.6 V vs. Li⁺/Li cutoff potential, while for the bare one the capacity decreases to 105 mAh/g under the same conditions.

Moreover, the thermal stability of the LiCoO₂ electrode at delithiated state measured by DSC, is improved by the surface modification with CeF₃ as compared with the bare layered sample.

The enhanced electrochemical performance of LiCoO₂ through surface coating should be contributed not only to the context of the structural stability of the core materials (thanks to the presence of nanosized-CeO₂), but also to the suppression of the interface reaction between the cathode and electrolyte, thus stabilizing the interface and protecting the cathode materials against HF attack in electrolyte. The ability for ceria

to acts as oxygen reservoir avoids the oxygen release from the LiCoO_2 structure and enhances their thermal properties at higher potential.

Therefore, the surface modification with nano film based Ce is an effective way to improve the electrochemical performance of lithium cobalt layered oxides.

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